REACTIONS OF HINDERED OLEFINS

BY

CHRIS EDWARD BEST

A.B., Marietta College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1943

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Introduction

The hindering influence of *ortho* substituents is generally associated with reactions that are additive in type and has been noted frequently in studies of aldehydes, ketones, esters, nitriles and other compounds in which the functional group contains a multiple linkage between carbon and a negative element. Very little attention, however, has been given to the influence of *ortho* substituents on reactions of carbon-to-carbon multiple linkages. To this end a study has been made of the effect of *ortho* substituents on the reactions of stilbene and 1,1-diphenylethylene.

The olefins selected for study were 1,2-dimesitylethylene, 1-mesityl-2-phenylethylene, 1-phenyl-2-(2,4,6-triisopropylphenyl)ethylene and 1-mesityl-1-phenylethylene.

Experimental and Discussion

1,2-Dimesitylethylene was made from mesital chloride by the coupling action of methylmagnesium iodide, the binary mixture, magnesium-magnesium iodide, or magnesium alone. The action of hydrogen sulfide and hydrogen chloride on mesitaldehyde converted it to a trimer of thiomesitaldehyde. Fusion of the trimer with copper-bronze produced 1,2-dimesitylethylene. The most satisfactory method of preparation, however, was by dehydration of 1,2-dimesitylethanol. The dehydration was best accomplished by a mixture of acetic anhydride and concentrated hydrochloric acid. Phosphorus pentoxide and sulfuric acid were also used as dehydrating agents. 1-Mesityl-2-phenylethylene and 1-phenyl-(2,4,6-triisopropylphenyl)ethylene were made by dehydration of the corresponding ethanols with sulfuric acid.

The olefins were treated with the following reagents: ozone, hydrogen in the presence of a metal, perbenzoic acid, alkali metals, potassium permanganate, the iodine-silver benzoate complex and phosphorus pentachloride.

In most of the tests normal reactions were observed. There were definite indications, however, that the *ortho* groups exerted a retarding influence.

Some abnormal results were obtained. 1,2-Dimesitylethylene and 1-mesityl-1-phenylethylene yielded small amounts of mesitol along with the normal ozonization products. The reaction between perbenzoic acid and 1,2-dimesitylethylene appeared to be complex and it was suspected that the mesityl radical was attacked. Investigation showed that mesitylene itself could be oxidized to mesitol by the action of perbenzoic acid.

VITA

The writer was born in Marietta, Ohio, on July 29, 1915. He received his elementary education in the public schools of that city and was graduated from Marietta High School in June, 1933. He entered Marietta College in the autumn of 1933 and was granted a Bachelor of Arts degree from that institution in June, 1937. From August, 1937 to September, 1939 he was employed in the Research Laboratory of the American Cyanamid Corporation. He entered the University of Illinois in the fall of 1939 where he held a teaching assistantship from September, 1940 to February, 1943.

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